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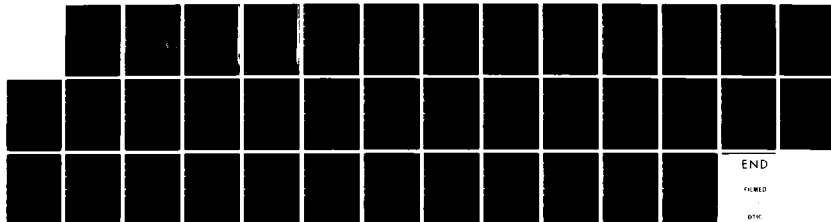
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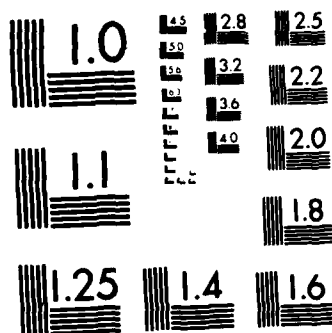
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The Driving-Force Dependence of Electrochemical Rate

Parameters: Origins of Anodic-Cathodic Asymmetries

for Metal Aquo Redox Couples

by

J. T. Hupp and M. J. Weaver

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Suitable theoretical formalisms are outlined for examining and predicting rate parameters for outer-sphere electron transfer in heterogeneous and homogeneous environments on a unified basis. They are utilized to calculate rate constants and activation parameters for 11 electrochemical and 45 homogeneous self-exchange and cross reactions involving transition-metal aquo, ammine, ethylenediamine, and polypyridine redox couples from the appropriate structural and thermodynamic data. Comparison between the calculated and experimental work-corrected rate constants, $k_{calc}$ and $k_{corr}$		

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respectively, indicates that almost uniformly  $k_{calc} \geq k_{corr}$ , the latter values being typically  $ca\ 10^{-10^3}$  fold smaller. These rate discrepancies are chiefly reflected in the activation entropies, although partly compensated by differences between the experimental and calculated activation enthalpies. Although the values of  $k_{calc}/k_{corr}$  depend somewhat upon the reaction environment as determined by the nature of the coordinated ligands and the metal surface, they are approximately independent of the magnitude of  $k_{corr}$  or the driving force. Taken together, these findings support the notion that the major origin of the discrepancies between  $k_{calc}$  and  $k_{corr}$  is associated with changes in local solvent structure when forming the precursor state. Nonadiabaticity may contribute importantly by necessitating that the reacting centers be in very close proximity. Reactions at "hydrophilic" metal surfaces, such as lead and gallium, that are known to strongly adsorb water molecules yield remarkably similar theory-experiment disparities to those seen with cationic coreactants in homogeneous solution. The markedly closer agreement obtained for some reactions at mercury is attributed to the relatively mild perturbation exerted by this metal surface upon the local solvent structure.

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THE DRIVING-FORCE DEPENDENCE OF ELECTROCHEMICAL  
RATE PARAMETERS: ORIGINS OF ANODIC-CATHODIC  
ASYMMETRIES FOR METAL AQUO REDOX COUPLES

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Abstract

The consequences of differences in the intramolecular force constants and the ionic entropies between the oxidized and reduced states of aquo redox couples upon their electrochemical kinetics are examined as a function of the driving force. A generalized harmonic oscillator model is utilized that involves estimating the activation barrier from the individual force constants in the oxidized and reduced states rather than employing average ("reduced") values. Noticeable asymmetry in the anodic and cathodic Tafel plots is predicted for redox couples having large (ca. twofold) differences in force constants, the plots being markedly more curved at anodic overpotentials. The calculated plots are in reasonable agreement with experimental Tafel plots determined previously for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  and  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$  at the mercury-aqueous interface. Comparisons are also presented between electrochemical "ideal" activation parameters determined for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  as a function of anodic and cathodic overpotentials and the corresponding parameters calculated from structural and thermodynamic data. Substantially smaller activation enthalpies are observed for  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation than for  $\text{Cr}(\text{OH}_2)_6^{3+}$  reduction; both are close to the theoretical predictions. The anodic activation enthalpies approach zero at moderate overpotentials even though the activation entropies remain large and negative. Parallels are also drawn with corresponding results and data interpretations of the driving-force dependencies for related homogeneous reactions.

## Introduction

We have recently reported and discussed an anomalous driving-force dependence of rate constants for the outer-sphere electrochemical reduction and oxidation involving metal (III)/(II) aquo couples of chromium, vanadium and europium at the mercury-aqueous interface.<sup>1,2</sup> The metal(III) reductions exhibit linear variations of the logarithm of the work-corrected rate constant,  $k_{\text{corr}}$ , with electrode potential (i.e. Tafel plots) over the entire accessible range of overpotentials (ca. 300 to 600 mV, depending on the reaction).<sup>1,3</sup> In contrast, the work-corrected Tafel plots for the corresponding metal(II) oxidations in hexafluorophosphate or perchlorate electrolytes are sharply curved at moderate overpotentials, yielding variations of  $\log k_{\text{corr}}$  with electrode potential at higher oxidation driving forces that are unexpectedly small<sup>1</sup> in comparison with the predictions of the usual harmonic oscillator treatment.<sup>4</sup> Similarly weak dependencies of the rate constants upon the thermodynamic driving force have been noted for a number of homogeneous bimolecular reactions involving oxidation of M(II) aqua complexes.<sup>2,5-8</sup>

The observed marked asymmetry of the anodic and cathodic Tafel plots contrasts the essentially symmetrical behavior predicted by the conventional theoretical relationships.<sup>1</sup> We have speculated that the major source of this asymmetry is associated with major differences in the short-range solvent polarization between the oxidized and reduced aquo species, possibly associated with a rearrangement step either before or after electron transfer.<sup>1</sup> However, the recent acquisition of reliable Raman spectral measurements for both M(III) and M(II) aquo complexes<sup>9</sup> along with the emergence of new metal-ligand bond length data<sup>10</sup> has prompted us to reexamine this problem. Specifically, these data indicate that the force constants for the totally symmetric metal-aquo stretching mode are expected to differ substantially (ca. twofold) between the oxidized and reduced forms for couples such as  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  which feature large changes ( $\sim 0.15$  to  $0.2 \text{ \AA}$ ) in the metal-ligand bond lengths, *ca.* Such force constant differences will yield noticeably

different free-energy parabolas for the oxidized and reduced forms for these reactions since a large portion of the free-energy barrier is associated with inner-shell (i.e. metal-ligand) reorganization. Such asymmetry in the free-energy curves for individual redox couples will often cancel for homogeneous reactions, especially those involving a structurally similar pair of redox couples. However, it can in principle yield significantly asymmetric activation energy-driving force [and hence  $\log k_{\text{corr}}$ -potential] plots for electrochemical reactions at anodic and cathodic overpotentials.<sup>4</sup> The extent of such asymmetry has been shown to be only minor at small overpotentials.<sup>4</sup> We have stated previously that this factor is much too small to account for the observed Tafel plot asymmetry.<sup>1</sup> However, more detailed consideration of the inner-shell reaction energetics on the basis of the recent structural data leads us to revise this conclusion.

The purpose of this communication is to examine in quantitative terms the predicted influence of differing metal-ligand force constants on such driving-force dependencies and the degree to which the experimental data can be accounted for on this basis. In addition, the electrochemical activation parameters for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  and  $\text{Eu}(\text{OH}_2)_9^{3+/2+}$  have been evaluated over a wide range of anodic and cathodic overpotentials and are compared with the corresponding theoretical predictions. Besides providing a more complete description of the driving-force dependent reaction energetics, such comparisons are of particular interest since the large (ca.  $200 \text{ J. deg}^{-1} \text{ mol}^{-1}$ ) differences in entropy between the oxidized and reduced aquo cations<sup>11</sup> yield very substantial differences in the redox thermodynamics at anodic and cathodic overpotentials.<sup>1</sup> Finally, some commonalities are explored between the driving-force dependence of redox reactivities for electrochemical and homogeneous processes.

### Driving-Force Dependence of Electrochemical Rate Constants

Figures 1 and 2 contain experimental Tafel plots for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  and  $\text{Eu}(\text{OH}_2)_9^{3+/2+}$ , respectively, over a range of anodic and cathodic overpotentials at the mercury-aqueous interface. These plots, which are taken from ref. 1, are shown as solid curves. Similar data have also been obtained for  $\text{V}(\text{OH}_2)_6^{3+/2+}$  although over a somewhat smaller overpotential range.<sup>1</sup> The dotted lines in Figs. 1 and 2 are the Tafel plots that would be obtained for the same value of  $k_{\text{corr}}$  at the formal potential,  $E_f$  (i.e. the "standard" rate constant  $k_{\text{corr}}^s$ ) if the transfer coefficient,  $\alpha_{\text{corr}}$ , equals 0.5 throughout the entire overpotential range. The transfer coefficient is defined as

$$\alpha_{\text{corr}} = \pm(RT/F)(d \ln k_{\text{corr}}/dE) \quad (1)$$

where the plus-minus sign refers to anodic and cathodic rate constants, respectively. The strongly asymmetric nature of the experimental anodic and cathodic Tafel plots is clearly seen by comparison with the dotted lines.

The conventional expression for electrochemical rate constants as a function of the overpotential<sup>4</sup> can be written for one-electron reactions as

$$k_{\text{corr}} = A \exp\{[-\lambda \pm F(E-E_f)]^2/4\lambda RT\} \quad (2)$$

where the plus-minus sign again refers to anodic and cathodic rate constants,  $A$  is a preexponential factor, and  $\lambda$  is the intrinsic reorganization energy. This last term is the free energy required to adjust the reactant nuclear coordinates so that they correspond to those of the product, but without electron transfer. The form of Eq. (2) clearly predicts symmetrical curved Tafel plots at anodic and cathodic overpotentials. This symmetry follows from the assumption contained in Eq. (2) that the force constants of the oxidized and reduced forms are equal; i.e. the reactant and product parabolas have identical shapes.

We and others have previously employed Eq. (2) (or equivalent relationships) for comparing the rate constant - overpotential dependence with the harmonic oscillator model.<sup>1,3,12</sup> It is conventional to determine  $\lambda$  from the experimental standard rate constant using Eq. (2) and to reinsert this quantity into Eq. (2) to find the predicted overpotential dependence of  $\log k_{\text{corr}}$  which is compared with the experimental data.<sup>1,3,12</sup> A somewhat different approach is used here whereby the predicted  $\log k_{\text{corr}}$  - overpotential dependences are obtained directly from *calculated* free-energy barriers derived from the known redox structural parameters. This procedure is now outlined.

The work-corrected rate constant can be expressed as<sup>13</sup>

$$k_{\text{corr}} = K_o v_n \Gamma_n \kappa_{\text{el}} \exp(-\Delta G^*/RT) \quad (3)$$

where  $K_o$  is the statistical part of the equilibrium constant for forming the precursor state from the bulk reactant,  $v_n$  is the nuclear frequency factor,  $\Gamma_n$  is the nuclear tunneling factor,  $\kappa_{\text{el}}$  is the electronic transmission coefficient, and  $\Delta G^*$  is the free energy of activation for the elementary electron-transfer step. Although the preexponential factors exert important influences upon the absolute magnitudes of  $k_{\text{corr}}$ , the dependence of  $k_{\text{corr}}$  upon the driving force is expected to arise almost entirely from variations in  $\Delta G^*$ . For the present purpose, it is particularly convenient to formulate  $\Delta G^*$  in terms of intrinsic reorganization energies for the forward and reverse directions,  $\lambda_f$  and  $\lambda_r$ , respectively, for the generalized reaction



Provided that the free energy-reaction coordinate profiles are quadratic in nature, values of  $\Delta G^*$  as a function of the free-energy driving force

$\Delta G^0 [= -F(E - E_f)]$  can be obtained from the solution to the following relations:<sup>14</sup>

$$\Delta G^* = \lambda_f X^2 \quad (5a)$$

$$\text{where} \quad \lambda_f X^2 = \lambda_r (1-X)^2 + \Delta G^\circ \quad (5b)$$

and  $X$  is a dimensionless parameter characterizing the nuclear coordinates of the transition state<sup>15</sup> (see Fig. 3). [For convenience, quantities such as  $\lambda_f$ ,  $\Delta G^*$ ,  $\Delta G^\circ$ , etc. refer here and below to the forward reaction, either cathodic or anodic, being considered even though the reduction process is commonly regarded as the "forward reaction", as in Eq. (4).] The combination of Eqs. (3) and (5) yields the simplified symmetrical relation Eq. (2) only for the special case when  $\lambda_f = \lambda_r = \lambda$ . However, when  $\lambda_f \neq \lambda_r$  they instead predict *nonsymmetrical*  $\log k_{\text{corr}}$  - overpotential plots in the anodic and cathodic directions. The latter will clearly apply when the force constants differ in the oxidized and reduced forms.

The various components of Eqs. (3) and (5) can be evaluated (or estimated) as follows. The forward and reverse reorganization energies for Eq. (4) can be separated into inner-shell (reactant bond distortional) and outer-shell (solvent reorganization) contributions according to

$$\lambda_f = \lambda_{is}^f + \lambda_{os} \quad (6a)$$

$$\lambda_r = \lambda_{is}^r + \lambda_{os} \quad (6b)$$

where  $\lambda_{is}^f$  and  $\lambda_{is}^r$  are the inner-shell reorganization energies associated with the reactant and product species, respectively.

These may be related to the corresponding force constant,  $f_i$ , for symmetrical bond stretching (or compression) of the  $i$ th bond, and the change in bond distance between the oxidized and reduced forms, by means of

$$\lambda_{is} = 0.5 \Sigma f_i \Delta a^2 \quad (7a)$$

$$\text{where} \quad f_i = 4 \pi^2 \nu_{in}^2 c^2 \mu \quad (7b)$$

where  $\nu_{in}$  is the bond vibrational frequency,  $c$  is the velocity of light, and  $\mu$  is the reduced mass of the vibrator.

The outer-shell reorganization energy,  $\lambda_{os}$ , will be assumed to be equal in the oxidized and reduced forms (*vide infra*). It is conventionally given by

$$\lambda_{os} = \frac{e^2 N}{2} \left( \frac{1}{r} - \frac{1}{R} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (8)$$

where  $e$  is the electronic charge,  $N$  is Avogadro's number,  $r$  is the reactant radius,  $R$  is the distance from the reactant to its image in the metal surface, and  $\epsilon_{op}$  and  $\epsilon_s$  are the optical and static dielectric constants, respectively. For the present aquo reactants,  $r$  was taken as  $3.25 \text{ \AA}^{10}$  and  $R$  as  $13 \text{ \AA}^{16}$ .

Values of  $\Delta G^*$  for the  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  couple were calculated as a function of overpotential using Eqs. (5) - (8), with  $\mu$  taken as the mass of the aquo ligand, along with the experimental values  $\nu_{III} = 543 \text{ cm}^{-1}$ ,  $\nu_{II} = 380 \text{ cm}^{-1}$ ,<sup>9,17</sup> and  $\Delta a = 0.20 \text{ \AA}^{10}$ . This yields inner-shell reorganization energies,  $\lambda_{is}^f$  and  $\lambda_{is}^r$ , equal to 223 and 110  $\text{kJ mol}^{-1}$ , respectively; and overall reorganization energies,  $\lambda_f$  and  $\lambda_r$ , of 310 and 197  $\text{kJ mol}^{-1}$ , respectively. The corresponding calculated values of  $k_{corr}$  were obtained by combining the values of  $\Delta G^*$  with numerical estimates of the preexponential factors in Eq. (3). Details concerning the physical significance of these quantities are given elsewhere.<sup>13,18,19</sup> The composite quantity  $K_o K_{el}$  was taken as 0.5<sup>8</sup>; similar values (within ca. twofold) are indicated from both experimental and theoretical lines of evidence.<sup>20</sup> The nuclear tunneling factor  $\tau_n$  was obtained from the driving-force dependent relationship of Holstein<sup>21</sup> as expressed conveniently by Sutin.<sup>22</sup> It is calculated to equal 3.4 at  $E=E_f$ , and depends only slightly upon overpotential in the range of interest here. The nuclear frequency factor  $\nu_n$  was determined as  $1.0 \times 10^{13} \text{ sec}^{-1}$  from the above stretching frequencies as described in ref. 13.

The resulting calculated values of  $\log k_{\text{corr}}$  against  $(E-E_f)$  for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  in both anodic and cathodic directions are plotted as dashed curves in Fig. 1. The standard rate constant,  $k_{\text{corr}}^s$ , obtained from theory is in almost exact agreement with the experimental value,  $3 \times 10^{-6} \text{ cm sec}^{-1}$ . Given the uncertainties and assumptions involved in deriving the former (probably ca.  $\pm 20$ -fold) this agreement is somewhat fortuitous. For convenience, the calculated and experimental values of  $k_{\text{corr}}^s$  are set exactly equal in Fig. 1 so to facilitate the comparison of the theoretical predictions for the driving-force dependence of  $k_{\text{corr}}$  with experiment.

The theoretical analysis for  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$  cannot be performed on the same quantitative basis as for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  since experimental data for  $v_{\text{III}}$ ,  $v_{\text{II}}$ , and  $\Delta a$  are unavailable. However, approximate calculations of the  $\log k_{\text{corr}}$  - overpotential plots for this couple may still be carried out. From the experimental standard rate constant,  $k_{\text{corr}}^s = 3 \times 10^{-5} \text{ cm sec}^{-1}$ , together with the theoretical value of  $\lambda_{\text{os}}$  assuming  $r = 3.5 \text{ \AA}$ ,  $R = 13 \text{ \AA}$  [ $87 \text{ kJ. mol}^{-1}$ , Eq. (8)], and noting that the reaction is likely to be nearly adiabatic ( $\kappa_{\text{el}} \sim 1$ ),<sup>23</sup> an intrinsic inner-shell barrier,  $\Delta G_{\text{int}}^*$  (i.e.  $\Delta G^*$  for  $\Delta G^\circ = 0$ ) of ca.  $30 \text{ kJ. mol}^{-1}$  is inferred. Since the interaction of  $\text{Eu}(\text{III})$  and  $\text{Eu}(\text{II})$  with the aquo ligands is predominantly electrostatic, the  $\text{Eu}-\text{OH}_2$  force constants should be approximately proportional to the ionic charge divided by the cation-aquo bond distance,  $a$ .<sup>24</sup> Given that  $a$  is likely to be about  $2 \text{ \AA}$ , and the difference in bond lengths between  $\text{Eu}(\text{III})-\text{OH}_2$  and  $\text{Eu}(\text{II})-\text{OH}_2$  is around  $0.22 \text{ \AA}$ ,<sup>23</sup> from the above values of  $\Delta G_{\text{int}}^*$  and  $\lambda_{\text{os}}$  and utilizing Eq. (5) for  $\Delta G^\circ = 0$  along with Eq. (6) leads to estimates of  $\lambda_{\text{in}}^{\text{Ox}}$  and  $\lambda_{\text{in}}^{\text{Red}}$  of  $170$  and  $95 \text{ kJ. mol}^{-1}$ , respectively. The overpotential dependence of  $\log k_{\text{corr}}$  for  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$  predicted by these parameters are shown as dashed curves in Fig. 2.

Comparison between the experimental and calculated Tafel plots for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  and  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$  in Figs. 1 and 2 reveals that the observed anodic-cathodic asymmetry is accounted for in part by the inclusion of larger force constants for the oxidized compared to reduced forms in the theoretical calculations. Thus these ratios of inner-shell force constants, estimated to be 2.05 and ca. 1.8 for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  and  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$ , respectively, yield noticeably smaller slopes in the Tafel plots at anodic as compared to cathodic overpotentials. Even though the predicted Tafel plots at cathodic overpotentials do exhibit some curvature, these are nevertheless closely similar to the essentially linear experimental plots in Figs. 1 and 2. At anodic overpotentials, the marked curvature in the experimental Tafel plots is roughly mimicked by the calculated plots, especially for  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation.

A comparison between the experimental and calculated transfer coefficients for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$ , derived from the slopes of the curves in Fig. 1 [Eq. (1)], is given in Table I. The calculated anodic and cathodic quantities,  $\alpha_{\text{calc}}^a$  and  $\alpha_{\text{calc}}^c$  respectively, were obtained from the dashed curves, i.e., using individual force constants. Although the changes in  $\alpha_{\text{calc}}^a$  and  $\alpha_{\text{calc}}^c$  with varying overpotential are similar, the former are substantially larger at a given overpotential, in harmony with the behavior of the corresponding experimental quantities  $\alpha_{\text{calc}}^a$  and  $\alpha_{\text{calc}}^c$  (Table I). In contrast, the transfer coefficient,  $\alpha_{\text{calc}}^{\text{sym}}$ , calculated from the conventional treatment [Eq. (2)] displays a symmetrical overpotential dependence, in marked disagreement with the observed behavior (Table I).<sup>1</sup> The values of  $\alpha_{\text{corr}}^a$  are nevertheless significantly smaller than  $\alpha_{\text{calc}}^a$  at large anodic overpotentials; this is also evident from the deviations between the solid and dashed curves in Fig. 1.

These residual discrepancies between theory and experiment at anodic overpotentials may be due to several causes. Most simply, the actual curvature in the experimental  $\log k_{\text{corr}}-E$  plots may be somewhat different than that shown in Figs. 1 and 2 due to possible potential-dependent errors in the application of double-layer corrections to the observed rate constants. Although the extent of this uncertainty is not large (around ca. twofold in  $\log k_{\text{corr}}$ ), it is greatest at the largest anodic overpotentials in view of the substantial anionic specific adsorption encountered even in hexafluorophosphate electrolytes.<sup>1</sup> However, it is more likely that the discrepancies are due largely to remaining inadequacies of the theoretical model. One possibility is that the metal-ligand vibrational modes are anharmonic. However, trial calculations using anharmonic Morse potentials in place of the

harmonic oscillator model [Eq. (7)] yielded almost imperceptible changes in the Tafel plots, at least for the conditions encountered in Fig. 1.<sup>25</sup> A more important factor, at least for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  is liable to reside in the above assumption that all the metal-ligand bonds are equivalent. A pair of *trans* chromium-oxygen bonds in  $\text{Cr}(\text{OH}_2)_6^{2+}$  are expected to be weaker, and therefore have smaller force constants, than the other four due to Jahn-Teller distortion. Since these bonds are also especially elongated,<sup>10</sup> they may well contribute importantly to the inner-shell barrier, yielding a more pronounced curvature in the calculated anodic Tafel plot.

As noted above, we previously attributed the observed Tafel plot asymmetry chiefly to the influence of short-range solvent polarization.<sup>1,3</sup> Although a large fraction of the asymmetry effect now appears to reside in the inner-shell barrier, the present analysis suggests a way in which the outer-shell reorganization can contribute as well. We assumed above that  $\lambda_{\text{os}}$  is equal for the reduction and oxidation directions; i.e. the outer-shell "force constant" is independent of the metal oxidation state. This follows from the simple dielectric continuum model used to estimate the outer-shell barrier. If reorganization of hydrogen-bonded outer-shell water molecules contributes significantly to the free-energy barrier, greater Tafel plot asymmetry should result since the effective force constants associated with such motions should also be larger in the higher oxidation state.<sup>3</sup> However, quantitative calculations of such effects are precluded at present due to the incompleteness of molecular structural information for the surrounding solvent.

With regard to recent provocative discussions,<sup>26,27</sup> we stress that it is necessary to include the outer-shell solvent contribution to the

reorganization barrier in order to obtain satisfactory agreement between the theoretical and experimental rate constants for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$ . This is also the case for a variety of other homogeneous and electrochemical reactions.<sup>19</sup> To illustrate this point for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$ , Fig. 1 also contains  $\log k_{\text{corr}} - E$  plots calculated by ignoring the solvent contribution (dotted-dashed lines). Although exhibiting very similar *dependences* of  $\log k_{\text{corr}}$  upon overpotential to that seen with the proper inclusion of the solvent reorganization component, the calculated values of  $\log k_{\text{corr}}$  are substantially (ca.  $10^4$  fold) larger than the experimental values.

In view of the continuing interest and speculation concerning the virtues of Tafel plots for examining some fundamental aspects of electrochemical kinetics,<sup>26,28,29</sup> it is worthwhile to note some more general implications of the foregoing. It is evident that the degree of curvature of the Tafel plots can be at least as sensitive to the degree of mismatch between the forward and reverse reorganization energies as to the absolute magnitude of these energies, and hence to the intrinsic barrier,  $\Delta G_{\text{int}}^*$ , and  $k_{\text{corr}}^S$ . It is therefore extremely dangerous to estimate intrinsic barriers from the curvature of Tafel plots.<sup>28,30,31</sup> Further, the Tafel plot shapes are not very diagnostic of the factors contributing to reactant activation, such as the role of solvent reorganization. A more valuable approach to examining such fundamental questions is to compare the absolute magnitudes of the calculated and experimental rate constants under well-defined conditions<sup>19</sup> rather than their dependence upon the thermodynamic driving force. Nevertheless, such Tafel comparisons do provide one means of evaluating more subtle driving-force dependent effects with the aim of "fine tuning" theoretical formulations.

## Driving-Force Dependence of Electrochemical Activation Parameters

Activation parameters clearly provide an additional measure of information on the reaction energetics beyond that yielded by rate measurements at a single temperature. These parameters can be particularly revealing, for example, of the solvational changes accompanying transition-state formation for simple redox reactions.<sup>32</sup> Two distinct types of activation parameters can usefully be distinguished for electrochemical reactions. The first type, the so-called "real" activation parameters, refer to the temperature dependence of the rate constant measured at a fixed overpotential.<sup>33</sup> The second type, so-called "ideal" activation parameters, are obtained from the temperature derivative evaluated at a fixed nonisothermal electrode potential.<sup>32-34</sup> The difference between these two types lies in the thermodynamic entropy change, the "reaction entropy"  $\Delta S_{rc}^\circ$ , brought about by electron transfer, i.e. the entropy difference between the reduced and oxidized forms of the redox couple.<sup>11</sup> This entropy change is associated with the temperature dependence of the standard electrode potential,<sup>11</sup> and gives rise to an inherent asymmetry of the electrochemical reaction energetics in the anodic and cathodic directions. Thus at the standard potential  $E_f$  where the free-energy driving force,  $\Delta G^\circ$ , necessarily equals zero, there will nevertheless be a nonzero (and often substantial) reductive enthalpic driving force,  $\Delta H_{rc}^\circ$ , since then  $\Delta H_{rc}^\circ = T\Delta S_{rc}^\circ$ .<sup>32-34</sup> Thus for  $\text{Cr}(\text{OH})_2^{3+/2+}$ ,  $\Delta S_{rc}^\circ = 205 \text{ J. K}^{-1} \text{ mol}^{-1}$ ,<sup>11</sup> and therefore at  $E_f$ ,  $\Delta H_{rc}^\circ = 61 \text{ kJ. mol}^{-1}$ . This is a key feature which sets apart electrochemical exchange reactions from the corresponding homogeneous self-exchange reactions; the latter are inherently symmetrical since they can be conceived as a coupled pair of electrochemical exchange reactions.<sup>2</sup>

The "ideal" activation parameters can be identified with the actual enthalpic and entropic barriers at the electrode potential at which they are evaluated. The cathodic and anodic "ideal" parameters will therefore differ markedly even at the standard electrode potential. The "real" activation parameters, on the other hand, contain a correction for the entropic driving force; they will necessarily be identical in the anodic and cathodic directions at the standard potential since the temperature-dependent anodic and cathodic rate constants will be equal under these conditions. The latter are therefore closely related to the activation parameters for homogeneous self-exchange reactions. However, the "ideal" parameters are more appropriate for the present purposes since they reveal the true asymmetric nature of the electrochemical reaction energetics.

Table II contains a comparison of experimental "ideal" enthalpies and entropies of activation,  $\Delta H_{\text{corr}}^*$  and  $\Delta S_{\text{corr}}^*$ , respectively, with the corresponding calculated quantities,  $\Delta H_{\text{calc}}^*$  and  $\Delta S_{\text{calc}}^*$ . The work-corrected activation enthalpies,  $\Delta H_{\text{corr}}^*$ , were obtained from<sup>35</sup>

$$\Delta H_{\text{corr}}^* = -R[\partial \ln k_{\text{corr}} / \partial (1/T)]_{E^{\text{ni}}} \quad (9)$$

where the temperature dependence of  $k_{\text{corr}}$  is evaluated at the constant nonisothermal cell potential  $E^{\text{ni}}$ . The values of  $k_{\text{corr}}$  were evaluated over the temperature range ca. 5-50°C; experimental details are given in ref. 32. At cathodic overpotentials the  $k_{\text{corr}}$  values were obtained from apparent rate constants measured in 1 M NaClO<sub>4</sub> (pH 2.5) as outlined in ref. 32. At anodic overpotentials, they were evaluated from rate data measured in 0.4 M KPF<sub>6</sub> (pH 2.5) as outlined in ref. 1. [Since quantitative double-layer data are not available for 0.4 M KPF<sub>6</sub> at potentials positive of the point of zero charge (where PF<sub>6</sub><sup>-</sup> specific adsorption occurs), the double-layer corrections are assumed to be independent of temperature. The

approximate validity of this assumption is supported by a similar finding for  $\text{Cr}(\text{OH}_2)_6^{3+}$  reduction<sup>32</sup> and the small absolute magnitude of the corrections required for  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation in 0.4 M  $\text{KPF}_6$ .<sup>1</sup> The work-corrected entropies of activation,  $\Delta S_{\text{corr}}^*$ , also listed in Table II, were obtained from the corresponding values of  $\Delta H_{\text{corr}}^*$  and  $k_{\text{corr}}$  at a given temperature, along with the above estimates of  $K_{\text{el}}^{\text{oc}}$  and  $v_n$  using

$$\Delta S_{\text{corr}}^* = R \ln k_{\text{corr}} - R \ln (K_{\text{el}}^{\text{oc}} v_n) + \Delta H_{\text{corr}}^* / T \quad (10)$$

Note that the temperature-dependent nuclear-tunneling factor  $\Gamma_n$  is contained within  $\Delta H_{\text{corr}}^*$  and  $\Delta S_{\text{corr}}^*$ , so that the latter can be regarded as "semiclassical" quantities.<sup>22</sup>

The corresponding calculated quantities,  $\Delta H_{\text{calc}}^*$  and  $\Delta S_{\text{calc}}^*$ , were obtained as follows. As shown in the Appendix, differentiation of Eq. (5) with respect to temperature yields an expression for the classical activation entropy (i.e. not containing the nuclear-tunneling correction):

$$\Delta S^* = \Delta S^\circ \lambda_f X [\lambda_r^2 + (\lambda_f - \lambda_r)(\Delta G^\circ + \lambda_r)]^{-1/2} \quad (11)$$

by assuming that  $d\lambda_f/dT = d\lambda_r/dT = 0$ ,<sup>36</sup> where  $\Delta S^\circ$  is the entropic driving force in the cathodic or anodic direction, as appropriate. An equivalent expression for  $\Delta S^*$  is simply (see Appendix)

$$\Delta S^* = \alpha \Delta S^\circ \quad (12a)$$

where the transfer coefficient,  $\alpha$ , as operationally defined by Eq. (1) is calculated from

$$\alpha = \lambda_f X (X \lambda_f + \lambda_r - X \lambda_r)^{-1} \quad (12b)$$

Although Eqs. (11) and (12a) are equivalent, the latter formulation is more revealing since it separates the simple phenomenological definition of  $\Delta S^*$

[Eq. (12a)] and its detailed calculation based on a harmonic oscillator treatment for  $\alpha$  [Eq. (12b)].

The classical activation enthalpy,  $\Delta H^*$ , is obtained from  $\Delta S^*$  together with the classical activation free energy from Eq. (5) using

$$\Delta H^* = \Delta G^* + T\Delta S^* \quad (13)$$

The calculated value of  $\Delta H^*$ ,  $\Delta H^*_{\text{calc}}$ , desired for comparison with the experimental value,  $\Delta H^*_{\text{corr}}$ , is obtained by including the temperature-dependent nuclear tunneling correction:

$$\Delta H^*_{\text{calc}} = \Delta H^* - R[d\ln\Gamma_n/d(1/T)] \quad (14)$$

Similarly, the corresponding calculated activation entropy can be obtained from

$$\Delta S^*_{\text{calc}} = \Delta S^* - R\ln\Gamma_n - (R/T)d\ln\Gamma_n/d(1/T) \quad (15)$$

The resulting values of  $\Delta H^*_{\text{calc}}$  and  $\Delta S^*_{\text{calc}}$  for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  are listed alongside the corresponding experimental estimates in Table II. The nuclear-tunneling corrections to  $\Delta H^*_{\text{calc}}$  and  $\Delta S^*_{\text{calc}}$  range from ca. -3.5 to -10 kJ. mol<sup>-1</sup> and -7 to -22 J. K<sup>-1</sup> mol<sup>-1</sup>, respectively, becoming more negative with increasing negative electrode potential.

Inspection of Table II reveals that the striking numerical differences in the calculated activation parameters for the anodic and cathodic directions brought about by the large reaction entropy for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  is matched to a large degree by the experimental values. This agreement extends, albeit approximately, to the very small values of  $\Delta H^*_{\text{corr}}$  and  $\Delta H^*_{\text{calc}}$  for  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation at large anodic overpotentials and their mild overpotential dependence in comparison with that for  $\text{Cr}(\text{OH}_2)_6^{3+}$  reduction at cathodic

overpotentials. Similar calculations for  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$  are not feasible since the required quantitative structural data unavailable for this couple. Nevertheless, the experimental values of  $\Delta H_{\text{corr}}^*$  and  $\Delta S_{\text{corr}}^*$  for  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$  also display striking differences in the anodic and cathodic directions as a consequence of the large  $\Delta S_{\text{rc}}^\circ$  value ( $195 \text{ J. K}^{-1} \text{ mol}^{-1}$  <sup>11</sup>) for this couple. In addition, similarly small and even negative values of  $\Delta H_{\text{corr}}^*$  for  $\text{Eu}(\text{OH}_2)_n^{2+}$  oxidation were obtained at anodic overpotentials [eg.  $\Delta H_{\text{corr}}^* = -5 \text{ kJ. mol}^{-1}$  at  $(E-E_f) = 400 \text{ mV}$ ].

An apparently unexpected finding which we alluded to earlier<sup>1</sup> is the observation of near zero activation enthalpies at anodic overpotentials even though the activation entropies remain large and negative under these conditions (Table II). Intuitively, one might expect the activation entropy to equal zero in the absence of an enthalpic barrier.<sup>1</sup> In order to examine this matter further, values of  $\Delta G_{\text{calc}}^*$ ,  $\Delta H_{\text{calc}}^*$ , and  $\Delta S_{\text{calc}}^*$  were calculated for  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation over a considerable range of free energy driving forces,  $\Delta G^\circ$ , corresponding to a much greater span of anodic overpotentials than can be examined experimentally. The resulting plots of  $\Delta G_{\text{calc}}^*$ ,  $\Delta H_{\text{calc}}^*$ , and  $\Delta S_{\text{calc}}^*$  against  $\Delta G^\circ$  are given in Fig. 4. (Nuclear tunneling corrections were omitted since these are small and the approximations inherent in their calculation become somewhat ambiguous for highly exoergonic reactions.<sup>38</sup>) Figure 4 indicates that  $\Delta H_{\text{calc}}^*$  decreases sharply and even assumes small negative values at substantially smaller driving forces than are necessary for  $\Delta G_{\text{calc}}^*$  to become zero. Indeed,  $\Delta H_{\text{calc}}^*$  attains a value of zero at two points, approximately when  $\Delta G^\circ = -(\lambda_f + 2T\Delta S^\circ)$  and when  $\Delta G^\circ = -\lambda_f$ , whereas  $\Delta G_{\text{calc}}^*$  and  $\Delta S_{\text{calc}}^*$  become zero only when  $\Delta G^\circ = -\lambda_f$ . The significance of negative activation enthalpies for related homogeneous reactions has been discussed by Marcus and Sutin.<sup>39</sup>

A related feature of Fig. 4 is the appearance of an enthalpic "inverted region", i.e. a realm of *increasing* activation enthalpy with increasing exoergonicity within the "normal free-energy region", i.e. where the activation free energy decreases with increasing driving force. It has been noted that the much-discussed free-energy inverted region<sup>40</sup> should be absent for electrochemical reactions at metal surfaces.<sup>41,42</sup> This is because oxidative electron transfer to metal energy states above the Fermi level, or reductive electron transfer from states below the Fermi level, will provide an activationless pathway even when  $-\Delta G^\circ$  exceeds  $\lambda_f$ . However, the *enthalpic* inverted region should nevertheless be observable for electrochemical reactions. It would be interesting to explore this possibility experimentally by selecting reactions with sufficiently negative values of  $\Delta S^\circ$  so that the anticipated enthalpic inverted region occurs at sufficiently large values of  $\Delta G_{\text{corr}}^*$  corresponding to measurably slow reaction rates.

It should be noted that the anodic-cathodic driving force asymmetry seen for the activation parameters has a different origin than that of the rate constants discussed above. Thus purely symmetrical Tafel plots will be predicted provided that  $\lambda_f = \lambda_r$  *irrespective* of major differences in the entropic and enthalpic components of these reorganization energies.<sup>1</sup> Nevertheless, these two types of driving force asymmetry are in a sense related since they both arise from equilibrium structural changes brought about by electron transfer. In addition, we have speculated that the especially small transfer coefficients observed at large anodic overpotentials (Figs. 1,2) may be connected with the occurrence of an enthalpically barrierless process (i.e.  $\Delta H_{\text{corr}}^* \sim 0$ ) under these conditions.<sup>1</sup> Although the above analysis based on force constant differences largely removes the need to invoke such "anomalous activation" mechanisms, such notions should nonetheless not be wholly discarded at this point.

# Parallel Reactivity Behavior for Homogeneous and Heterogeneous Processes

The foregoing demonstrates that the chief property of simple electrochemical reactions which leads to unusual driving force-dependent reactivities is their inherent chemical asymmetry. In this regard interfacial redox reactions have much in common with homogeneous cross reactions between structurally diverse redox centers, and in fact are more akin to these than to homogeneous self-exchange reactions. As an illustration, consider the  $V(OH_2)_6^{3+/2+}$  couple. The  $V(OH_2)_6^{3+/2+}$  homogeneous self-exchange reaction is a completely symmetrical process and is therefore necessarily isoenergetic as well as thermo-neutral and isoentropic. In contrast,  $V(OH_2)_6^{3+/2+}$  electrochemical exchange is characterized by net  $\Delta S^\circ$  and  $\Delta H^\circ$  values of  $-155 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $-46 \text{ kJ mol}^{-1}$ , respectively,<sup>11</sup> for the oxidation reaction at the standard potential (i.e. for  $\Delta G^\circ = 0$ ). These thermodynamic changes are closely shared by the oxidation of  $V(OH_2)_6^{2+}$  by  $Cr(bpy)_3^{3+}$  in homogeneous aqueous solution (bpy = 2,2'-bipyridine), since the formal potentials of the reacting redox couples are virtually identical ( $-480 \text{ mV vs. s.c.e.}^{11,43}$ ), and  $\Delta S_{rc}^\circ$  for  $Cr(bpy)_3^{3+/2+}$  is close to zero ( $15 \text{ J. K}^{-1} \text{ mol}^{-1}$ <sup>43</sup>). [The values of  $\Delta S^\circ$  and  $\Delta H^\circ$  are deduced to be  $-140 \text{ J. K}^{-1} \text{ mol}^{-1}$  and  $-41 \text{ kJ. mol}^{-1}$ , respectively.] It is not surprising, therefore, that cross reactions between aquo and low-spin polypyridine complexes exhibit similarly "unusual" activation parameters to electrochemical reactions involving the former reactants.<sup>5</sup> For example, the highly exoergonic oxidations of  $Fe(OH_2)_6^{2+}$  by  $Ru(bpy)_3^{3+}$ ,  $Ru(phen)_3^{3+}$  and  $Fe(phen)_3^{3+}$  are characterized by small negative activation enthalpies and large negative activation entropies.<sup>44-6</sup> It has been shown that the substantial negative entropic driving force for these reactions ( $\Delta S^\circ \approx -175 \text{ J K}^{-1} \text{ mol}^{-1}$ <sup>12</sup>) can account in broad terms for this kinetic behavior on the basis of the measured rate parameters for the parent self-exchange reactions.<sup>39</sup>

Moreover, comparably "anomolous" rate-driving force dependencies to those discussed here for electrochemical oxidations have also been observed for a number of homogeneous oxidations of aquo complexes.<sup>2</sup> Analysis of the driving-force dependencies of homogeneous reactivity is complicated by the need to account for activation of the reducing, as well as oxidizing, redox center. Low-spin polypyridine complexes provide particularly useful coreactants in this regard<sup>2</sup> since the small entropic changes<sup>43</sup> and intrinsic activation barriers<sup>47</sup> that are characteristic of such couples enable the reaction energetics to be dominated by the other redox center. In this respect such polypyridine reactants provide similar redox characteristics to metal surfaces. Although the "overpotential" provided by the former is fixed by its formal potential, driving force dependencies can nevertheless be scrutinized by selecting a related series of polypyridine oxidants having a suitable range of formal potentials.<sup>44</sup>

The dependence of homogeneous reactivities upon the driving force has often been discussed<sup>2,5,48,49</sup> in terms of observed deviations from the "Marcus cross relationship"<sup>4</sup>

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (16a)$$

where 
$$f = (\log K_{12})^2 / [4 \log(k_{11}k_{22}/A^2)] \quad (16b)$$

Here  $k_{12}$  is the rate constant for a cross reaction having an equilibrium constant  $K_{12}$  from the known self-exchange rate constants,  $k_{11}$  and  $k_{22}$ , for the constituent redox couples. Since Eq. (16) is derived by assuming that the force constants for the oxidized and reduced form of both reacting couples are equal,<sup>4,50</sup> progressively larger deviations from this relation are expected as the driving force is increased. When  $\lambda_f < \lambda_r$  (as for aquo

complex oxidations), the observed values of  $k_{12}$  are expected to be progressively smaller than those predicted from Eq. (16) as  $K_{12}$  increases.<sup>50</sup> Such considerations are entirely analogous to those considered above for electrochemical reactions. Thus the symmetrical Tafel relations obtained from the harmonic oscillator model with  $\lambda_f = \lambda_r$  [Eq. (12)] can be derived from Eq. (16) by noting that a metal surface can be regarded formally as a coreactant with variable driving force and zero intrinsic barrier; (i.e. having a "self-exchange rate constant" equal to the preexponential factor, A).

Chou et al regarded the deviations from Eq. (16) due to unequal force constants as being too small to account for the observed discrepancies for a number of homogeneous cross reactions, including several oxidations of aquo complexes.<sup>5</sup> Undoubtedly other factors, such as additional components of work terms, nonadiabaticity,<sup>5,48,49</sup> use of inappropriate self-exchange rate constants,<sup>51</sup> etc. also contribute importantly in many cases. Nevertheless, the above analysis clearly indicates that force constant differences can provide significant driving force-dependent deviations from Eq. (2) and therefore from Eq. (16). Indeed, by employing the free-energy form of Eq. (16) we have demonstrated that the observed driving force-dependent deviations observed for homogeneous oxidations of aquo complexes are quantitatively consistent with the corresponding deviations for the electrooxidation reactions that are discussed here.<sup>2</sup>

The present analysis focusses attention on aquo redox couples since structural as well as extensive rate parameter-overpotential data are available for these systems. Nevertheless, such rate-driving force asymmetries should be observed for any redox couple with suitably large force constant differences between the oxidized and reduced forms, providing that inner-shell reorganization provides an important contribution to the activation barrier.

These two factors will tend to occur together since it is anticipated that redox couples having such large force constant differences will also exhibit sizable bond-length changes upon electron transfer, and hence have large inner-shell barriers. Since such large structural changes commonly give rise to rapid irreversible chemical steps following electron transfer, the number of chemically reversible couples having the required properties may be relatively small. Nevertheless, the possible occurrence of such Tafel plot asymmetry, yielding otherwise unexpected Tafel linearity or curvature, should be borne in mind when examining the electrochemical kinetics of reactions involving coupled chemical steps, including those involving proton transfer such as proton electroreduction.

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## APPENDIX: Equivalence of Equations 11 and 12

The free energy expression

$$\Delta G^* = X^2 \lambda_f \quad (5a)$$

may be differentiated with respect to temperature to yield:

$$\Delta S^* = -2\lambda_f X \, dX/dT \quad (A1)$$

By solving Eq. 5 one obtains for X:

$$X = \{-\lambda_r + [\lambda_r^2 + (\lambda_f - \lambda_r)(\Delta G^\circ + \lambda_r)]^{1/2}\} (\lambda_f - \lambda_r)^{-1} \quad (A2)$$

Assuming that  $d\lambda/dT = 0$ , differentiation of Eq. A2 yields:

$$dX/dT = -\frac{1}{2} \Delta S^\circ [\lambda_r^2 + (\lambda_f - \lambda_r)(\Delta G^\circ + \lambda_r)]^{-1/2} \quad (A3)$$

Substitution of Eq. A3 into Eq. A1 yields Eq. 11:

$$\Delta S^* = \Delta S^\circ X \lambda_f [\lambda_r^2 + (\lambda_f - \lambda_r)(\Delta G^\circ + \lambda_r)]^{-1/2} \quad (11)$$

Rearranging Eq. A2 we find that:

$$[\lambda_r^2 + (\lambda_f - \lambda_r)(\Delta G^\circ + \lambda_r)]^{1/2} = X(\lambda_f - \lambda_r) + \lambda_r \quad (A4)$$

and

$$[\lambda_r^2 + (\lambda_f - \lambda_r)(\Delta G^\circ + \lambda_r)]^{-1/2} = (X\lambda_f + \lambda_r - X\lambda_r)^{-1} \quad (A5)$$

Incorporating this result into Eq. 11 yields:

$$\Delta S^* = \Delta S^\circ \lambda_f X (X\lambda_f + \lambda_r - X\lambda_r)^{-1} \quad (A6)$$

From Eq. 5b one can obtain (noting that  $d\lambda/dX = 0$ ):

$$d\Delta G^\circ/dX = 2(X\lambda_f + \lambda_r - X\lambda_r) \quad (A7)$$

From Eq. 5a one finds that

$$d\Delta G^*/dX = 2X \lambda_f \quad (A8)$$

In view of Eqs. A7 and A8, Eq. A6 may be rewritten as

$$\Delta S^* = \Delta S^\circ (d\Delta G^*/dX) (d\Delta G^\circ/dX)^{-1} = \Delta S^\circ d\Delta G^*/d\Delta G^\circ \quad (A9)$$

Noting that the transfer coefficient  $\alpha$  is defined as  $d\Delta G^*/d\Delta G^\circ$ , we conclude that

$$\Delta S^* = \alpha \Delta S^\circ \quad (12a)$$

At first sight, Eq. (12a) appears to be simply the entropic analog of the free-energy expression

$$\Delta G^* = \Delta G_{int}^* + \alpha \Delta G^\circ \quad (A10)$$

where  $\Delta G_{int}^*$  is the "intrinsic" free-energy barrier, i.e. that which remains in the absence of the free-energy driving force  $\Delta G^\circ$ . [Equation (A10) is the most general form of the dependence of the activation barrier upon the driving force.] Indeed, the above assumption,  $d\lambda/dT = 0$ , made in deriving Eq. (12a) is equivalent to asserting that the intrinsic entropic barrier equals zero. However, a difference between the forms of Eqs. (12a) and (A10) is that the transfer coefficient appearing in the former is the usual *differential* quantity,  $\alpha_d$ , defined by Eq. (1) or, equivalently, by  $\alpha_d = d\Delta G^*/d\Delta G^\circ$ , whereas that occurring in the latter is an *integral* quantity defined by  $\alpha_i = (\Delta G^* - \Delta G_{int}^*)/\Delta G^\circ$ . Generally  $\alpha_d$  will differ from  $\alpha_i$  when the Tafel plots are curved, i.e. when  $\alpha$  depends upon  $\Delta G^\circ$ .<sup>3</sup> This distinction between the forms of Eqs. (12a) and (A10) arises since the former can be obtained by taking the temperature derivative of the latter at a constant Galvani potential (i.e. nonisothermal cell potential), whereupon  $d\alpha_i/dT \neq 0$ .

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36. This is tantamount to assuming that the classical intrinsic activation entropy  $\Delta S_{\text{int}}^{\ddagger}$ , i.e. the activation entropy that remains in the absence of an entropic driving force, equals zero. Although this is only approximately true, generally  $\Delta S_{\text{int}}^{\ddagger} < 10 \text{ J. K}^{-1} \text{ mol}^{-1}$  for electrochemical reactions in aqueous solution.<sup>37</sup>

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38. Following current thinking,<sup>40c</sup> the magnitude of the nuclear tunneling correction will be maximized when the enthalpic, rather than the free-energy, driving force is zero. However, the relevant driving force is that associated with the particular (inner- or outer-shell) mode being considered. Since the partitioning of either the enthalpic or the free-energy driving force into inner- and outer-shell components is fraught with difficulties, the accurate prediction of the effective dependence of  $\Gamma_n$  upon the cathodic and anodic overpotential, is precluded at present. Nevertheless, approximate calculations for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  indicate that  $\Gamma_n$  depends only slightly on the overpotential increasing monotonically with increasing negative electrode potential over the range considered in Fig. 1; (3.4 for  $E=E_f$ , 2.0 at  $(E-E_f) = 800$  mV, and 4.0 at  $(E-E_f) = -600$  mV.
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TABLE I Dependence of Experimental and Calculated Transfer Coefficients for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  on Anodic as compared to Cathodic Overpotential

$\pm(E-E_f)^a$ mV	Anodic		Cathodic		$\alpha_{\text{calc}}^{\text{sym } f}$
	$\alpha_{\text{corr}}^a$	$\alpha_{\text{calc}}^a$	$\alpha_{\text{corr}}^c$	$\alpha_{\text{calc}}^c$	
0		0.45		0.55	0.50
200	0.35	0.40	0.50	0.52	0.46
400	0.22	0.36	0.49	0.47	0.42
600	0.20	0.33	~0.48	0.43	0.38
800	~0.19	0.29			0.34

<sup>a</sup> Anodic or cathodic overpotential.

<sup>b</sup> Anodic experimental transfer coefficient corrected for work terms, at listed overpotentials; data from ref. 1.

<sup>c</sup> Anodic transfer coefficient, calculated using individual force constants for  $\text{Cr}^{\text{III}}\text{-OH}_2$  and  $\text{Cr}^{\text{II}}\text{-OH}_2$  bonds as described in text.

<sup>d</sup> Cathodic experiment transfer coefficient corrected for work terms, at listed overpotentials; data from ref. 3.

<sup>e</sup> Cathodic transfer coefficient, calculated using individual force constants for  $\text{Cr}^{\text{III}}\text{-OH}_2$  and  $\text{Cr}^{\text{II}}\text{-OH}_2$  bonds as described in text.

<sup>f</sup> Anodic or cathodic transfer coefficient calculated assuming equal force constants in oxidized and reduced forms [Eq. (2)].

TABLE II Comparison of Experimental and Calculated Activation Parameters for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  at Cathodic and Anodic Overpotentials

$E^{ni} - E_f^a$ mV	$\Delta H_{\text{corr}}^*{}^b$ kJ mol <sup>-1</sup>	$\Delta H_{\text{calc}}^*{}^c$ kJ mol <sup>-1</sup>	$\Delta S_{\text{corr}}^*{}^d$ J. K <sup>-1</sup> mol <sup>-1</sup>	$\Delta S_{\text{calc}}^*{}^e$ J. K <sup>-1</sup> mol <sup>-1</sup>
$\text{Cr}(\text{OH}_2)_6^{3+}$ reduction				
-350	63	64	68	80
-300	68	66	68	80
-250	73	70	68	82
-200	78	74	66	85
-150	84	77	65	88
$\text{Cr}(\text{OH}_2)_6^{2+}$ oxidation				
350	11	17	-85	-90
450	9	15	-90	-85
550	7	13	-92	-80
650	5	12	-95	-78
750	4	10	-92	-75
850	3	9	-90	-70
900	2	8	-85	-66

Footnotes to Table II

- <sup>a</sup> Overpotential, where  $E^{ni}$  is nonisothermal cell electrode potential with reference electrode held at 25°C, and  $E_f$  is the formal potential for  $\text{Cr}(\text{OH}_2)_6^{3+/2+}$  (-660 mV) at 25°C.
- <sup>b</sup> Experimental work-corrected "ideal" enthalpy of activation for  $\text{Cr}(\text{OH}_2)_6^{3+}$  reduction (cathodic overpotentials) or  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation (anodic overpotentials). Former evaluated using 1 M  $\text{NaClO}_4$  supporting electrolyte,<sup>32</sup> and latter using 0.4 M  $\text{KPF}_6$ .
- <sup>c</sup> Corresponding calculated "ideal" enthalpy of activation, obtained as described in text.
- <sup>d</sup> Work-corrected "ideal" entropy of activation for  $\text{Cr}(\text{OH}_2)_6^{3+}$  reduction (cathodic overpotentials) or  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation (anodic overpotentials), obtained from corresponding values of  $\Delta H_{\text{corr}}^*$  and  $k_{\text{corr}}$  as outlined in text.
- <sup>e</sup> Corresponding calculated "ideal" entropy of activation, obtained as outlined in text.

## Figure Captions

### Figure 1

Plots of the logarithm of the rate constant,  $\log k$ , for  $\text{Cr}(\text{OH}_2)_6^{3+}$  reduction and  $\text{Cr}(\text{OH}_2)_6^{2+}$  oxidation at cathodic and anodic overpotentials, respectively, against the electrode potential,  $E$ . Solid curves are the experimental work-corrected Tafel plots at mercury-aqueous interface, taken from refs. 1 and 3. Dotted line is anodic Tafel plot corresponding to a transfer coefficient of 0.50. (Experimental cathodic Tafel plot has slope of 0.50.) Dashed lines are anodic and cathodic Tafel plots calculated using individual force constants for  $\text{Cr}^{\text{III}}\text{-OH}_2$  and  $\text{Cr}^{\text{II}}\text{-OH}_2$  bonds (see text for details). Dotted-dashed curves are corresponding calculated Tafel plots, but assuming that the outer-shell reorganization energy equals zero.

### Figure 2

As Fig. 1, but for  $\text{Eu}(\text{OH}_2)_n^{3+/2+}$ .

### Figure 3

Schematic representation of forward and reverse reorganization energies,  $\lambda_f$  and  $\lambda_r$ , for case when the force constants for the product bonds are greater than for the reactant bonds. The nuclear reaction coordinate is given by the dimensionless parameter  $X$  in Eq. (5).

### Figure 4

Calculated free energy, enthalpic, and entropic barriers;  $\Delta G^*$ ,  $\Delta H^*$ , and  $T\Delta S^*$ , respectively; for  $\text{Cr}(\text{OH}_2)_6^{2+}$  electrooxidation as function of free-energy driving force,  $\Delta G^\circ [= -F(E-E_f)]$ , using Eqs. (5), (6), (8), (11), and (13) assuming that  $2\lambda_f = \lambda_r$ .

